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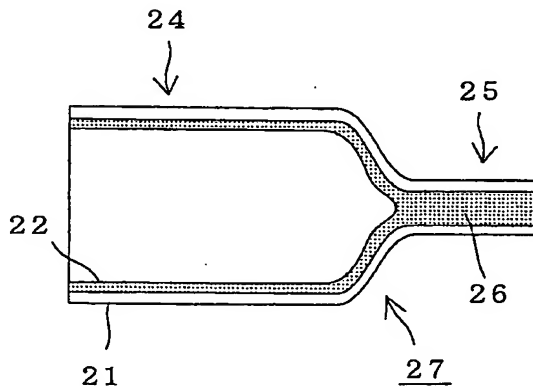
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のガイダンスノート」を参照。(54) Title: ADHESIVE COMPOSITION, PROCESS FOR PRODUCING THE SAME, MOLDED OBJECTS, AND PROCESS
FOR PRODUCING HEAT-SHRINKABLE TUBE

(54) 発明の名称: 接着性組成物、その製造方法、成形物、及び熱収縮性チューブの製造方法

(57) Abstract: An adhesive composition which com-
prises 100 parts by weight of a fluoropolymer and 2 to 30
parts by weight of an unsaturated compound having at
least one polar group selected from the group consisting
of epoxy and carboxy and in which the fluoropolymer
has been grafting-modified with the unsaturated com-
pound having one or more polar groups by irradiation
with an ionizing radiation; and molded objects, such as
a heat-shrinkable tube and a heat-shrinkable cap, which
each has a layer of the adhesive composition.(57) 要約: フッ素系ポリマー100重量部に対し
て、エポキシ基及びカルボキシル基からなる群
より選ばれる少なくとも一種の極性基を含有する
不飽和化合物を2~30重量部の割合で含有し、
かつ電離放射線の照射により該フッ素系ポリ
マーが該極性基含有不飽和化合物によりグラ
フト変性されている接着性組成物、その製造方
法、該接着性組成物からなる層を備えた熱収縮

性チューブ、熱収縮性キャップなどの成形物。

WO 2005/005564 A1

Specification

Adhesive composition, its preparation process, molded articles and
method for producing heat shrink tube

Field of the Invention

This invention relates to a hot melt type adhesive composition improved in adhesion to metals and thermal resistance.

This invention also relates to a molded article having an adhesive layer made of the adhesive composition, such as a multilayered heat shrink tube and a heat shrink cap each having an adhesive layer made of the adhesive composition on its inner layer.

This invention also relates to a process for preparing such adhesive composition and multilayered heat shrink tube.

The adhesive composition, multilayered heat shrink tube and a heat shrink cap can be used advantageously for protection, connection and hermetic sea of electric wire, wire harness (knitted wires) and piping for which high continuous thermal resistance of higher than 150°C is requested.

Background of the Invention

In automobile and aerospace industries, parts such as electric wire, wire harness and piping must be resistance to high temperature environment. Therefore, adhesive composition used in such industries for protection, connection and hermetic sea must have higher thermal resistance of higher than 150°C.

For example, a multilayered heat shrink tube used in the automobile industries has an inner layer of hot melt adhesive for bundling wire harness, connection, and protection of end terminals from a view point of insulation and water-proof.

The heat shrink tube having the hot-melt adhesive layer on its inside is used also in connection hydraulic lines made of copper, iron and stainless steel for waterproofing and protection against corrosion.

In use, the heat shrink tube having the hot-melt adhesive layer on its inside shrinks around an object to be protected and the hot-melt adhesive fuse so that spaces between the tube and the object is filled with fused the hot-melt adhesive, resulting in realizing a protection against penetration of water and corrosive gas or waterproof and anti-corrosion.

It is know that the heat shrink tube can be made of such materials as polystyrene, polyvinyl chloride, cross-linked polyethylene, fluorine resin and fluorine rubber. Fluorine resin and fluorine rubber are usually used for such applications where higher continuous thermal resistance of 150 °C is required.

It is also know that the hot melt adhesive used in inner layer of heat shrink tube can be made of such resin composition as dimer acid type polyamide resin, polyamide 6,

polyamide 10 and polyamide 11. These hot melt adhesive is coated on inner surface of the heat shrink tube.

The continuous use temperature of these hot melt adhesive, however, is at most about 105°C and hence can not be used in the applications in which the continuous thermal resistance of 150°C or more is required. In fact, adhesion was lost when the conventional heat shrink tube having these hot-melt adhesive on its inner layer was exposed to high temperature environment higher than 150°C.

JP-A1-5-57791 proposes two-layer structure consisting of a heat cross-linked shrink tube of fluorine resin and an inner layer of fluorine resin composition layer having high fluidity and low melt point. This heat shrink tube, however, is satisfied the waterproof and anti-corrosion, because the fluorine resin composition for inner layer have no adhesive property although spaces between the tube and the object is filled with fused fluorine resin composition.

Description of the Invention

A problem to be solved by the present invention is to provide a hot melt type adhesive composition improved in adhesion to metallic objects (including an object having a metallic surface) and thermal resistance.

Another problem to be solved by the present invention is to provide a molded article having an inner layer of an adhesive composition improved in adhesion to the article and thermal resistance.

A special problem to be solved by the present invention is to provide a multilayered heat shrink tube and a heat shrink cap having an inner layer of an adhesive composition improved in adhesion to articles including metallic objects to the article and thermal resistance.

Further problem to be solved by the present invention is to provide a method for producing the adhesive composition and multilayered heat shrink tube.

Inventors of this application studied to solve the technical problems and found that the hot melt type adhesive composition improved in adhesion to objects including metallic object and thermal resistance and have higher thermal resistance of higher than 150°C can be obtained by adding unsaturated compound having at least one polar group chosen from a group comprising epoxy group and carboxyl group to fluorine polymer such as fluorine resin and fluorine rubber and by irradiating the resulting fluorine composition with ionized radiation so that the fluorine composition is graft-denatured with the unsaturated compound having polar group.

The hot melt type adhesive composition according to the present invention can be used as adhesive for a molded article such as heat shrink tube. In particular, a multilayer heat shrink tube comprising a heat shrink tube made of radiation cross-linkable composition containing fluorine polymer and polyfunctional monomer and an adhesive composition layer deposited on its inner surface can improve

waterproof and anti-corrosion ness of a variety of objects including metallic objects, because the adhesive composition fill a clearance between the object and the heat shrink tube when the tube shrinks under heat and shows improve adherence to the object.

A heat shrink cap can be obtained by heat-sealing an end of a heat shrink tube having the above-mentioned layered structure. The heat shrink cap according to the present invention can be used for hermetic seal of terminals of electric wire and wire harness.

This invention is completed based on this knowledge.

(Claims are repeated and hence is not repeated)

Brief Description of Drawings

Fig. 1 is a schematic drawing showing a multilayer heat shrink tube according to the present invention.

Fig. 2 illustrates a step for producing the multilayer heat shrink tube.

Fig. 3 is a cross section of the multilayer heat shrink tube according to the present invention.

Fig. 4 illustrates a step for carrying out a capping of a terminal of cable.

Best mode for carrying out the Invention

1. Adhesive Composition

In the invention, at least one fluorine polymer chosen from a group comprising fluorine resin and fluorine rubber is used as polymer base of the adhesive composition.

The fluorine resin may be thermoplastic fluorine resins such as polyvinylidene fluoride (PVdF) which is homopolymer of vinylidene fluoride (VdF); PVdF type co- polymer such as vinylidene fluoride (VdF) - tetrafluoroethylene (TFE) and/or hexafluoropropylene (HFP) such VdF-TFE copolymer, VdF-HFP copolymer, VdF-TFE-HFP terpolymer; copolymer (ETFE) of ethylene and TFE or terpolymer containing third component; copolymer (ECTFE) of ethylene and chlorotrifluoroethylene (CTFE) and or terpolymer (ECTFE) containing third component; copolymer with (FEP) of TFE and HFP; and copolymer (PFA) of TFE and perphloro alkyl vinyl ether such as perfluoromethylvinylether (PFMVE).

The fluorine rubber may be vinylidene fluoride type fluorine rubber (FKM) such as copolymers of vinylidene fluoride (VdF) and hexafluoropropylene fluoride (HFP) tetrafluoroethylene (TFE), pentafluoropropylene (PFP), perfluoromethylvinylether (PFMVE) and chlorotrifluoroethylene (CTFE), such as VdF-HFP fluorine rubber, VdF-HFP-TFE fluorine rubber, VdF-PFP fluorine rubber, VdF-PFP-TFE fluorine rubber, VdF-PFMVE-TFE fluorine rubber, VdF-CTFE fluorine rubber; and tetrafluoroethylene -propylene fluorine rubber (TFE-P) of TFE and propylene (P) and its terpolymer (TFE-P) containing third component added to TFE-P. It is also possible to use

thermoplastic fluorine rubber having fluorine resin as hard segment and fluorine rubber as soft segment.

The fluorine resin and fluorine rubber can be used each alone or in combination. Or, fluorine resin and fluorine rubber can be blended. In the case where fluorine resin and fluorine rubber are blended, both can be blended in a weight ratio of 5:95 to 95:5, preferably of 10:90 to 90:10. Optionally, other thermoplastics, rubber and thermoplastic elastomer can be blended together provide that thermal resistance and adhesive property are not spoiled.

In this invention, the fluorine polymer is graft-denatured with unsaturated compound ("polar-group containing unsaturated compound" hereinafter) containing at least one polar group chosen from a group consisting of epoxy group and carboxyl group.

The epoxy group containing unsaturated compound may be glycidyl ester of unsaturated carboxylic acid such as glycidyl acrylate, glycidyl methacrylate and p-styryl glycidyl carboxylate; allyl compound glycidyl isocyanate such as diaryl monoglycidyl isocyanate, monoallyl diglycidyl isocyanate; monoglycidyl ester or poly glycidyl ester of unsaturated polycarboxylic acid such as end-bicyclo[2, 2, 1] hepto-5-en -2, 3-dicarboxylic acid and end-cis-bicyclo[2, 2, 1] hepto-5-en-2-methyl-2, 3-dicarboxylic acid; unsaturated glycidylethers (allyl glycidyl ethers) such as allyl glycidyl ether, 2-methyl allyl glycidyl ether, glycidyl ether of o-allyl phenol, glycidyl ether of m-allyl phenol and glycidyl ether of p- allylphenol; 2-(o-vinyl phenyl) ethylene oxide, 2-(p-vinyl phenyl) ethylene oxide, 2-(o-allyl phenyl) ethylene oxide, 2-(p-allyl phenyl) ethylene oxide, 2-(o-vinyl phenyl) propylene oxide, 2-(p-vinyl phenyl) propylene oxide, p-glycidyl styrene, 3, 4-epoxy-1-butene, 3, 4-epoxy-3-methyl-1-butene, 3, 4-epoxy-1-pentene, 3, 4-epoxy-3-methyl-1-pentene, 5, 6-epoxy-1-hexene, vinyl cyclohexane mono-oxide and allyl -2, 3-epoxy cyclopentyl ether.

The epoxy group containing unsaturated compound can be any compound that has a carbon-carbon unsaturated bond and at least one epoxy group in its chemical structure.

Among epoxy group containing unsaturated compounds, allyl glycidyl ester, allyl glycidyl isocyanates, monoglycidyl ester or poly glycidyl ester of unsaturated polycarboxylic acid and allyl glycidyl ethers are preferable because graft- addition can be effected at higher conversion ratio by the exposure to ionizing radiation. The epoxy group containing unsaturated compound can be used alone or in combination.

The carboxyl group containing unsaturated compound may be unsaturated carboxylic-acid such as acrylic acid, methacrylic acid, crotonic acid, maleic acid fumaric acid and itaconic acid; acid-anhydrides of unsaturated dicarboxylic-acid such as maleic anhydride, itaconic anhydride and succinic anhydride and anhydride of monocarboxylic acid such as crotonic anhydride. Other compounds such as acid halide, amide, imide, ester of unsaturated carboxylic acid also can be used.

The carboxyl group containing unsaturated compound can be any compound that

has a carbon-carbon unsaturated bond and at least one carboxyl group in its chemical structure. The carboxyl group containing unsaturated compound can be used alone or in combination.

Among carboxyl group containing unsaturated compounds, anhydrides and compounds having carbon-carbon double bond are preferable because graft-addition can be effected at higher conversion ratio by the exposure to ionizing radiation. Maleic anhydride is more preferable.

If necessary, both of carboxyl group containing unsaturated compound and epoxy group containing unsaturated compound can be used together.

The polar group containing unsaturated compound is used in a proportion of 2 to 30 parts by weight, preferably 2.5 to 25 parts by weight with respect to 100 parts by weight of fluorine polymer. If the proportion of the polar group containing unsaturated compound is not within this range, adhesive property to metals become insufficient.

The ionizing radiation can be carried out by electron ray, gamma ray, X-ray, alpha ray, ultraviolet ray or the like. From a viewpoint of industrial use, transparency thickness for ionizing radiation and graft-reaction rate, electron ray and gamma ray are desirable. Especially, accelerated electron ray is preferable.

In the invention, graft reaction can be carried out by irradiating fluorine polymer compound containing fluorine polymer and polar-group containing unsaturated compound containing at least one polar group chosen from epoxy group and carboxyl group. The resulting graft-denatured fluorine polymer shows improved adhesion to metals and also shows fluidity under heat.

A dose of the exposure of ionizing radiation is preferably in a range of 20 to 700 kGy. If the dose is less than 20 kGy, initial adhesive property is not sufficient. On the other hand, if the dose exceeds 700kGy, the adhesive resin composition decomposes remarkably and thermal resistance is spoiled.

The degree of grafting can be adjusted by controlling a blending ratio of the polar-group containing unsaturated compound to the fluorine polymer and by changing the dose of radiation of ionizing radiation.

The adhesive composition of this invention can contain further, if necessary, fillers such as an inorganic filler, antioxidant, stabilizer, lubricant, ultraviolet ray absorbent, light stabilizer, copper inhibitor, cross linking agent, cross linking aide, bridge inhibitor, vulcanizing agent, vulcanization accelerator, scorch retarder, anti-ozonant, silicone, plasticizer, softener, foaming agent and antiseptics.

From a viewpoint of thermal stability of the additive component, it is preferable to add antioxidant such as pentaerythritol-tetrakis [3-(3, 5-di t-butyl-4-hydroxyphenyl) propionate], tetrakis-[methylene-3-(3', 5'-di t-butyl-4'-hydroxyphenyl) propionate] methane, 1, 1, 3-tris-(2-methyl-4-hydroxy-5-t-butylphenyl) butane, 4, 4'-butylidenebis-(3-methyl-6-t-butylphenol) and tris-(3, 5-di t-butyl-4-hydroxybenzyl) isocyanurate.

The antioxidant can be used in a proportion of 0.1 to 5 parts by weight, desirably 0.2 to 3 parts by weight, more desirably 0.3 to 2 parts by weight.

The fluorine polymer composition containing fluorine polymer and unsaturated compound containing at least one polar group chosen from epoxy group, and a carboxyl group is irradiated with ionizing radiation. The fluorine polymer composition may be shaped previously into a sheet or film form, coating layer or other forms. For example, if a film-like fluorine polymer composition is irradiated with ionizing radiation, a dry film having adhesive property can be obtained. This dry film can be used as an adhesive film which is inserted between for example metallic object and another object and is heat-sealed under heat and pressure.

When the fluorine polymer composition layer is deposited as an inner layer of a heat shrink tube and is irradiated with ionizing radiation, a multilayered heat shrink tube is obtained. This multilayered heat shrink tube has the adhesive composition layer possessing adhesive property and melting fluidity (hot melt property).

The adhesive composition containing fluorine polymer according to the present invention can be prepared by

- (i) preparing adhesive composition, containing 100 parts by weight of fluorine polymer and 2 to 30 parts by weight of unsaturated compound having at least one polar group chosen from a group comprising epoxy group and carboxyl group, and then
- (ii) said fluorine polymer is graft-denatured with said unsaturated compound grafted by exposure to ionized radiation, optionally after said composition is shaped.

The dose of the exposure of ionizing radiation is desirably in the aforementioned range.

The adhesive composition according to this invention has the continuous use temperature of higher than 150°C and the initial adhesive strength to stainless plate, copper plate, iron plate and aluminum plate of higher than 1.0 kg/cm determined by the T-peel test method of "initial adhesion test with metal plate (peel speed of 50mm/min) shown in Example 1, and the adhesion strength to the metal plates after degradation aging test effected at 150°C for 3000 hours in gear oven of higher than 1.0 kg/cm.

2. Molded articles

The molded articles of this invention can have any shape and be made of any material but preferably made of synthetic resin, more preferably made of fluorine polymer. The molded article has an adhesive layer of the adhesive composition at a desired position.

The molded articles can be a multilayer heat shrink tube having an adhesive layer of the adhesive composition on its inner surface. The multilayer heat shrink tube is preferably made of ionizing radiation cross-linkable composition containing fluorine polymer and polyfunctional monomer and is shrunk by ionizing radiation.

The molded articles can be a heat shrink cap prepared by heat-sealing an open end of a heat shrink tube having an adhesive layer on its inner surface

The multilayer heat shrink tube having an adhesive layer on its inside of this

invention can be produced by

- (1) preparing a two-layered heat shrink tube by co-extruding an inner layer of the fluorine polymer composition, and an outer layer of radiation-crosslinkable composition containing 100 parts by weight of fluorine polymer and 2 to 30 parts by weight of unsaturated compound having at least one polar group chosen from a group comprising epoxy group and carboxyl group,
- (2) irradiating said two-layered heat shrink tube with ionizing radiation to effect radiation-induced crosslinking of said outer layer and to effect graft-denaturing of said inner layer of fluorine polymer composition,
- (3) expanding the tube radially under heat, and
- (4) cooling the tube to fix its configuration expand radially.

A main body (outer layer) of the heat shrink tube of fluorine polymer can be same as those used for preparing the adhesive composition. Among them fluorine resin or fluorine rubber containing vinylidene fluoride unit are desirable.

The fluorine resin and fluorine rubber may be polyvinylidene fluoride (PVdF) which is homopolymer of vinylidene fluoride (VdF); PVdF type co- or ter-polymer such as vinylidene fluoride (VdF) - tetrafluoroethylene (TFE) and/or hexafluoropropylene (HFP) such VdF-TFE copolymer, VdF-HFP copolymer and VdF-TFE-HFP terpolymer. A proportion of vinylidene fluoride unit in PVdF copolymer is higher than 60%, preferably higher than 65 % ; more preferably higher than 70 % by weight.

Polyfunctional monomer is a compound containing two or more polymerizable carbon-carbon double bonds. Examples are allyl compounds such as diallyl phthalate, triaryl cyanurate, and triallyl isocyanurate; methacrylate compounds, such as ethylene glycol dimethacrylate, trimethylol propanetrimethacrylate, trimethylolethane methacrylate, trimethylol propane acrylate, trimethylol propane methacrylate, trimethylol triacrylate and tetramethylolmethane tetraacrylate; vinyl compounds such as divinylbenzene.

Among these polyfunctional monomers, trimethylolpropanetrimethacrylate and triallyl isocyanurate are preferable from a viewpoint of cross-linkability, thermal resistance and dispersibility to fluorine polymer.

Polyfunctional monomer can be used alone or in combination of more than two compounds. A proportion of the polyfunctional monomer is, with respect to 100 parts by weight of fluorine polymer, 0.1 to 20 parts by weight, preferably 0.3 to 10 parts by weight, more preferably 0.5 to 5 parts by weight.

The multilayer heat shrink tube can be produced by co-extruding (A) radiation-induced crosslinkable composition containing fluorine polymer and polyfunctional monomer and (B) fluorine polymer composition containing fluorine polymer and polar-group containing unsaturated compound to obtain a tubular two-layered product having an outer layer of the radiation cross-linkable composition layer (A) and an inner layer of fluorine polymer composition layer (B).

Then, the tubular two-layered product is irradiated with ionizing radiation to

effect cross-linking of the outer layer of the radiation cross-linkable composition layer (A) and to effect graft-denaturing of the inner layer of fluorine polymer composition (B).

In the radiation, it is desirable to adjust the condition of ionizing radiation to the inner layer of fluorine polymer composition (B) to 20 to 700kGy. Therefore, the dose of ionizing radiation for crosslinking the radiation cross-linkable composition layer (A) is preferably selected in a range of 20 to 700kGy.

Then, the irradiated tubular two-layered product is expanded radially under heat and a shape is fixed or immobilized by cooling. Expansion of the irradiated tubular two-layered product is effected generally at 100 to 250°C, preferably at 130 to 200°C, more preferably 140 to 180°C and usually at an expansion ratio of 1.1 to 5 times, preferably 1.2 to 4 times and more preferably 1.3 to 3 times. The expansion can be effected by feeding compressed air into the tubular molded product. The cooling solidification after expansion can be effected for example by immersing the tubular molded product in water at ambient temperature (25°C) or lower.

The multilayer heat shrink tube of this invention has an outer layer of crosslinked and expanded fluorine polymer composition, and hence will be shrunk to its original diameter when heated. This heating condition is 100 to 250°C, preferably 130-200°C, more preferably 140-180°C. Under this heating condition, the adhesive composition layer of inner layer melt, flow and adhere to an object. Therefore, the clearance between the multilayer heat shrink tube of this invention tube and the object can be filled completely with the adhesive composition. Still more, penetration of air, chemicals and water can be prevented due to excellent adhesive property.

Since the radiation-induced crosslinkable composition containing fluorine polymer of the outer layer is cross-linked, this layer neither fuses nor decomposes under the heating conditions for usual heat shrinking. In order that the outer layer does not fuse under usual temperature for shrinking operation, it is desirable to use such fluorine polymer as having a melting point which is higher than 100°C, preferably 140 to 200 °C, more preferably 140 to 200°C.

On the other hand, the adhesive composition of inner layer is not cross-linked and hence shows melt-fluidity although it is graft-denatured due to exposure to ionizing radiation. In order that the adhesive composition of the inner layer shows such melt-fluidity under the heating condition for effecting heat-shrink of the outer layer, the fluorine polymer constituting the adhesive composition is preferably such a fluorine resin as having a melting point of 80 to 140°C, preferably 90 to 130°C from a viewpoint of heat-resistant and melt-fluid balance, or is such a fluorine rubber as having a Mooney viscosity (ML_{1+10} , 121°C) of 50 to 70, preferably, 10 to 50. It is possible to adjust melting fluidity and thermal resistance, by blending fluorine resin with fluorine rubber.

Fig. 1 illustrates a schematic drawing of the multilayer heat shrink tube of this invention. The multilayer heat shrink tube of this invention consists of an outer layer 1 as a body of a heat shrink tube and an adhesive composition layer 2 arranged inside.

A heat shrink cap has the same lamination as this multilayer heat shrink tube but one open end is heat-sealed so that the adhesive composition is fused to close the end.

Figs. 2 and 3 show how to produce the heat shrink cap. As is shown in Fig. 2, the heat shrink cap of this invention consists of an outer layer 21 as a body of a heat shrink tube and an adhesive composition layer 22 arranged inside and has a predetermined length. A non-adhesive rod 23 is inserted from one opening of the heat shrink tube to an intermediate position or the rod is covered with the heat shrink tube. The non-adhesive rod 23 can be made of non-adhesive material such as polytetrafluoroethylene.

The heat shrink tube is heated under the condition shown in Fig. 2, so that a portion where the rod does not exist is heat-shrunk and the adhesive composition of inner layer fuses and closes this portion. Then, the rod is drawn out to obtain a the heat shrink cap shown in Fig. 3 having a filled portion 26 in which the heat shrink tube 21 shrunk and filled with and closed by the adhesive composition fused and an opposite portion 24 communicated with an open end.

Fig. 4 illustrates how to use this heat shrink cap. In this example, an assembly 28 of three coated electric wires 29 is sealed by the heat shrink cap. Exposed terminal conductors 30 are clipped by a metal connecting sleeve 31 and the heat shrink cap 27 is inserted onto it. What is necessary is just to insert the heat shrink cap 27 from one end of the cables 28 because another side is closed. Then, the heat shrink cap is heated so that the cap is heat-shrunk and seal the ends of cables.

[Examples]

Example and Comparative Examples will be given below more concretely but this invention is not limited these Examples.

Physical properties shown in Example and Comparative Examples are determined by methods described in Example 1.

Example 1

1. Preparation of sample for evaluating the adhesive compositions

Followings were melt-kneaded in a biaxial extruder at 180°C :

100 parts by weight of polyvinylidene fluoride type terpolymer (Mitsubishi Chemical, trade name "KYNAR 9300": melting point = 100°C, melt flow rate (MFR) = 120g/min (190°C, under a load of 2.16 kg)

3 parts by weight of glycidyl methacrylate as epoxy group containing unsaturated compound, and

0.5 parts by weight of pentaerythritol - tetrakis [3-(3, 5-di-t-butyl-4-hydroxyphenyl) propionate] as anti-oxidant.

The resulting product was pelletized to obtain pellets from which a sheet having a thickness of 1 mm was prepared by a hot press. This sheet was irradiated with electron ray of acceleration voltage of 2 MeV at a doze of 60 kGy to prepare a sample

for evaluation.

2. Initial Adhesion with Metal Plate

A rectangular strip having a width of 20mm x a length of 100mm was cut from the evaluation sample and was laminated onto a metal plates (stainless steel, copper plate, iron plate, aluminum plate) having the sample dimensions as the evaluation sample at 160°C, under a pressure of 2 Mpa for 2 minutes by a hot press. The peel strength was measured by T-peel test (peel speed of 50mm/min). The initial adhesive strength was determined from an average (n= 3).

It is known that the adhesive strength of higher than 1.0 kg/cm is required to assure waterproof at the connection for a heat shrink tube having such a structure that a hot-melt adhesive layer is arranged on its inner layer currently used for connecting wire harness. Therefore, in this invention, the criterion of success or failure of the adhesive strength between adhesive and metal is selected whether it is higher than 1.0 kg/cm or not

3. Heat-resistant

Heat resistant was evaluated by the sample method (adhesive strength) as above after the metal plates were aged or accelerated-deteriorated in a gear oven n at 150°C for 3000 hours.

Heat resistant was determined by taking into consideration the long-term thermal resistance of ISO standard. In fact, it can be judged that a continuous use temperature is higher than 150°C, if the adhesive strength of the sample after accelerated-degradation was higher than 1.0 kg/cm.

4. Production of Multilayer Heat Shrink Tube

Two-layered structure tube (inner diameter of 2.5 mm, outer diameter of 6.5 mm, and a thickness of the inner layer is 1 mm) was produced by co-extruding following two layers from a cross head of following two melting extruders at 180°C:

- 1) a melting extruder for outer layer (40 mmφ, full flight type of Hastelloy type) which extruded a radiation-induced crosslinkable composition comprising 100 parts by weight of polyvinylidene fluoride type copolymer [Mitsubishi Chemical, trade name "KAYNR 2800"; melting point = 148°C, MFR = 0.2g /10 minutes (230°C, 2.16 kg)] and 1 part by weight of trimethylolpropanetrimethacrylate, and
- 2) another melting extruder for inner layer (30 mmφ, full flight type of Hastelloy type) which extruded pellets of the composition containing the terpolymer prepared in Example 1, glycidyl methacrylate and antioxidant.

The resulting two-layered tube was irradiated with electron ray at acceleration voltage of 2 MeV at a dose of 60 kGy to effect crosslinking of the outer layer and graft-denaturation of the inner layer.

The resulting crosslinked tube was pre-heated in a thermostat at 170°C for 3

minutes and then was expanded by feeding compressed air into the tube to an outer diameter of 7.0 mm. Then, the tube was taken out of the thermostat immediately and was immersed in water to set or solidify the shape. The resulting multilayer heat shrink tube was cut to a length of 60 mm.

5. Evaluation of Waterproof

Seven fluorine electric wires of Sumitomo Electric Industries Ltd (ARX-3KAI) each having an outer diameter of 1.25 mm (conductor = 12/0.18, thickness = 0.25mm) and four fluorine electric wires of Sumitomo Electric Industries Ltd (ARX-3KAI) each having an outer diameter of 1.48 mm (conductor = 11/0.16, thickness = 0.43 mm) were jointed. Onto the joint, the multilayer heat shrink tube of above-mentioned (length of 60 mm) was put and the multilayer heat shrink tube was shrunk by using batch type contraction processing machine of Sumitomo Electric Industries Ltd (temperature of 520°C, 20 seconds) to obtain a joint sample.

Air-leak was tested by immersing this joint part of the multilayer heat shrink tube into water at a depth of 30 mm under a surface (7 twisted copper wires above water, 4 twist iron wires were in water) and a pressurization air of 49 kPa was applied to for 30 seconds from the upper part. When there is no air leak, it is considered as "success" while when there is air leak, it is judged that waterproof is inadequate so that it is considered as "failure" (the initial waterproof).

The same waterproof evaluation was effected after degrading of the joint under the condition of 150°C, for 3000 hours (the waterproof after degradation).

6. Results

From the aforementioned evaluation tests, it was revealed that the adhesive composition of Example 12 had the initial adhesive strength of higher than 1.0 kg/cm and passed the initial waterproof evaluation test. Still more, it showed such high thermal resistance of more than 1.0 kg/cm of adhesion strength even after degradation test 150°C, for 3000 hours. Therefore, this product passed the waterproof evaluation after degradation. Result is shown in Table 1.

Examples 2 to 12

Procedure of Example 1 was repeated except the fluorine polymer used for the adhesive composition, the polar-group containing unsaturated compound, blending ratio and the doze of exposure to accelerated electron ray were changed as are shown in Table 1 and the adhesive composition and the multilayer heat shrink tube were evaluated by the similar methods.

Although not shown in Table 1, 0.5 parts by weight of pentaerythritol-tetrakis [3-(3, 5-di-t-butyl-4-hydroxyphenyl)propionate] was blended as anti-oxidant to each adhesive composition to 100 parts by weight of the fluorine polymer.

Evaluation revealed that all adhesive compositions of Examples 2 to 12 had the

initial adhesive strength of higher than 1.0 kg/cm and that the initial waterproof evaluation using the multilayer heat shrink tube having the adhesive composition in its inner layer passed. Still more, it showed such high thermal resistance of more than 1.0 kg/cm of adhesion strength even after degradation test 150°C, for 3000 hours. Therefore, these products passed the waterproof evaluation after degradation. Result is summarized in Table 1.

[Table 1]

(note)

- (*1) PVdF-1 :
polyvinylidene fluoride type terpolymer [Mitsubishi Chemical, trade name "KAYNR 9300"; melting point = 100°C, MFR = 120g/min (190°C, 2.16kg)]
- (*2) PVdF-2:
polyvinylidene fluoride type copolymer [Mitsubishi Chemical, trade name "KAYNR 7200"; melting point = 120°C, MFR=2g/min (230°C, 2.16kg)]
- (*3) FKM-1:
fluorine rubber [E. I. du Pont de Nemours, trade name "Viton E-430"; fluorine content = 66%, Mooney viscosity (ML₁₊₁₀, 121°C) = 20]
- (*4) FKM-2 :
ternary fluorine rubber [E. I. du Pont de Nemours, trade name "Viton B-50"; fluorine content = 68%, Mooney viscosity (ML₁₊₁₀, 121°C) = 30]

Examples 13 to 24

Procedure of Example 1 was repeated except blends of the fluorine resin and fluorine rubber were used as fluorine polymer for the adhesive composition and the polar-group containing unsaturated compound, blending ratio and the dose of exposure to accelerated electron ray were changed as are shown in Table 2 and the adhesive composition and the multilayer heat shrink tube were evaluated by the similar methods.

Although not shown in Table 2, 0.5 parts by weight of pentaerythritol-tetrakis [3-(3, 5-di-t-butyl-4-hydroxyphenyl)propionate] was blended as anti-oxidant to each adhesive composition to 100 parts by weight of the fluorine polymer.

Evaluation revealed that all adhesive compositions of Examples 13 to 24 had the initial adhesive strength of higher than 1.0 kg/cm and that the initial waterproof evaluation using the multilayer heat shrink tube having the adhesive composition in its inner layer passed. Still more, it showed such high thermal resistance of more than 1.0 kg/cm of adhesion strength even after degradation test 150°C, for 3000 hours. Therefore, these products passed the waterproof evaluation after degradation. Result is summarized in Table 2.

[Table 2]

(note)

- (*1) PVdF-1:
Mitsubishi Chemical, trade name "KAYNR 9300" [melting point = 100°C, MFR = 120g/min (190°C, 2.16kg)]
- (*2) PVdF-2:
Mitsubishi Chemical, trade name -- "KAYNR 7200" [melting point = 120°C degree-C, MFR=2g/min (230°C, 2.16kg)]
- (*3) FKM-1:E.
I. du Pont de Nemours, trade name "Viton E-430" [fluorine content = 66%, Mooney viscosity (ML₁₊₁₀, 121°C) = 20]
- (*4) FKM-2 :
E. I. du Pont de Nemours, trade name "Viton B-50" [fluorine content = 68%, Mooney viscosity (ML₁₊₁₀, 121°C) = 30]

Comparative Examples 1 to 12

Procedure of Example 1 was repeated except the fluorine polymer used for the adhesive composition, the polar-group containing unsaturated compound and blending ratio were changed as are shown in Table 3 but accelerated electron ray was not irradiated and the adhesive composition and the multilayer heat shrink tube were evaluated by the similar methods.

Although not shown in Table 3, 0.5 parts by weight of pentaerythritol-tetrakis [3-(3, 5-di-t-butyl-4-hydroxyphenyl)propionate] was blended as anti-oxidant to each adhesive composition to 100 parts by weight of the fluorine polymer.

Evaluation revealed that all adhesive compositions of Comparative Examples 1 to 12 had poor the initial adhesive strength of lower than 1.0 kg/cm. Therefore, degradation test at 150°C, for 3000 hours was not effected.

The multilayer heat shrink tube having the adhesive composition in its inner layer of Comparative Examples 1 to 12 failed to the initial waterproof evaluation test. It is clear that these products can not passed the waterproof evaluation test after degradation. Result is summarized in Table 3.

[Table 3]

(note)

(*1) PVdF-1:

Mitsubishi Chemical, trade name "KAYNR 9300" [melting point =100°C, MFR = 120g/min (190°C, 2.16kg)]

(*2) PVdF-2:

Mitsubishi Chemical, trade name -- "KAYNR 7200" [melting point =120°C degree-C, MFR=2g/min (230°C, 2.16kg)]

(*3) FKM-1:E.

I. du Pont de Nemours, trade name "Viton E-430" [fluorine content =66%, Mooney viscosity (ML₁₊₁₀,121°C) =20]

(*4) FKM-2 :

E. I. du Pont de Nemours, trade name "Viton B-50" [fluorine content =68%, Mooney viscosity (ML₁₊₁₀,121°C) =30]

Comparative Examples 13 to16 and Reference Example 1

Procedure of Example 1 was repeated except the fluorine polymer used for the adhesive composition and the dose of exposure to accelerated electron ray were changed as are shown in Table 4 but the polar-group containing unsaturated compound was not used to produce the multilayer heat shrink tube were evaluated by the similar methods.

Although not shown in Table 4, 0.5 parts by weight of pentaerythritol-tetrakis [3-(3, 5-di-t-butyl-4-hydroxyphenyl)propionate] was blended as anti-oxidant to each adhesive composition to 100 parts by weight of the fluorine polymer.

Evaluation revealed that all adhesive compositions of Examples 2 to 12 had the initial adhesive strength of higher than 1.0 kg/cm and that the initial waterproof evaluation using the multilayer heat shrink tube having the adhesive composition in its inner layer passed. Still more, it showed such high thermal resistance of more than 1.0 kg/cm of adhesion strength even after degradation test 150°C, for 3000 hours. Therefore, these products passed the waterproof evaluation after degradation. Result is summarized in Table 4.

As Reference Example, the adhesive composition using the fluorine polymer was replaced by a hot-melt adhesive consisting mainly of dimer acid polyamide resin and the dose of electron ray was changed to 200 kGy to produce and evaluate the multilayer heat shrink tube by the same method as Example 1. Results are summarized in Table 4.

Evaluation revealed that all adhesive compositions of Comparative Examples 13 to 16 had poor the initial adhesive strength of lower than 1.0 kg/cm. Therefore, degradation test at 150°C, for 3000 hours was not effected.

The multilayer heat shrink tube having the adhesive composition in its inner layer of Comparative Examples 13 to 16 failed to the initial waterproof evaluation test. It is clear that these products can not passed the waterproof evaluation test after degradation.

In case of Reference Example 1 in which the hot-melt adhesive of dimer acid type polyamide resin was used, the adhesive strength to metal at the initial stage was such excellent as higher than 1.0 kg/cm and a heat-shrinkable tub having this hot-melt adhesive in inner layer passed the waterproof evaluation test.

However, this hot-melt adhesive degraded seriously when aged at 150°C, for 3000 hours in a gear oven and almost lost adhesive property. Therefore, its adhesive strength was estimated as 0 kg/cm, and hence this tube did not pass the waterproof evaluation test after degradation.

[Table 4]

Table 4

		Comparative Example				Reference Example 1
		1 3	1 4	1 5	1 6	
PVdF-1 (*1)		100	—	—	—	Hot-melt adhesive composed mainly of dimer acid type polyamide resin
PVdF-2 (*2)		—	100	—	—	—
FKM-1 (*3)		—	—	100	—	—
FKM-2 (*4)		—	—	—	100	—
glycidyl methacrylate		—	—	—	—	—
diallyl monoglycidyl isocyanate		—	—	—	—	—
maleic anhydride		—	—	—	—	—
doze of electron beam	kGy	700	200	400	20	200
initial adhesion strength kg/cm	stainless steel	0.0	0.0	0.0	0.0	1.4
	copper	0.0	0.0	0.0	0.0	2.3
	iron	0.0	0.0	0.0	0.0	1.7
	aluminum	0.0	0.0	0.0	0.0	1.5
Initial water-proof of heat-shrink tube		Failure				Success
Adhesion strength after 150°C × 3000 kg/cm	stainless steel	—	—	—	—	0.0
	copper	—	—	—	—	0.0
	iron	—	—	—	—	0.0
	aluminum	—	—	—	—	0.0
Water-proof after degradation		Failure				Failure

(note)

(*1) PVdF-1:

Mitsubishi Chemical, trade name "KAYNR 9300" [melting point = 100°C, MFR = 120g/min (190°C, 2.16kg)]

(*2) PVdF-2:

Mitsubishi Chemical, trade name -- "KAYNR 7200" [melting point = 120°C degree-C, MFR=2g/min (230°C, 2.16kg)]

(*3) FKM-1:E.

I. du Pont de Nemours, trade name "Viton E-430" [fluorine content = 66%,

Mooney viscosity ($ML_{1+10,121^{\circ}C}$) =20]

(*4) FKM-2 :

E. I. du Pont de Nemours, trade name "Viton B-50" [fluorine content =68%,
Mooney viscosity ($ML_{1+10,121^{\circ}C}$) =30]

Comparative Examples 17 to 32

Procedure of Example 1 was repeated except blends of the fluorine resin and fluorine rubber were used as fluorine polymer for the adhesive composition and the polar-group containing unsaturated compound and blending ratio and the dose of accelerated electron ray were changed as are shown in Table 5. The adhesive composition and the multilayer heat shrink tube were evaluated by the similar methods.

Although not shown in Table 5, 0.5 parts by weight of pentaerythritol-tetrakis [3-(3, 5-di-t-butyl-4-hydroxyphenyl)propionate] was blended as anti-oxidant to each adhesive composition to 100 parts by weight of the fluorine polymer.

Evaluation revealed that all adhesive compositions had poor the initial adhesive strength of lower than 1.0 kg/cm for under no irradiation of accelerated electron ray (Comparative Examples 17 to 28) and for no use of polar-group containing unsaturated compound (Comparative Examples 29 to 32). Therefore, degradation test at $150^{\circ}C$, for 3000 hours was not effected.

The multilayer heat shrink tube having the adhesive composition in its inner layer of Comparative Examples 17 to 32 failed to the initial waterproof evaluation test. It is clear that these products can not passed the waterproof evaluation test after degradation. Result is summarized in Table 5.

[Table 5]

Table 5

		Comparative Examples															
		17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
		50	80	-	-	70	40	70	40	-	-	-	-	50	80	-	-
	PvAF-1(*1)	-	-	80	50	-	-	-	-	80	50	40	70	-	-	80	50
	PvAF-2(*2)	50	-	20	-	30	-	30	-	20	-	60	-	50	-	20	-
	FKM-1(*3)	-	20	-	50	-	60	-	60	-	50	-	30	-	20	-	50
	FKM-2(*4)	30	2	10	25	-	-	-	-	-	-	-	-	-	-	-	-
	glycidyl methacrylate	-	-	-	-	10	5	-	-	-	-	15	3	-	-	-	-
	diallyl monoglycidyl isocyanate	-	-	-	-	-	-	15	5	10	2.5	-	-	-	-	-	-
	maleic anhydride	0	0	0	0	0	0	0	0	0	0	0	0	30	650	300	150
	Dose of electron beam	0.3	0.1	0.2	0.2	0.1	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.0	0.0	0.0	0.0
	stainless steel	0.2	0.1	0.1	0.1	0.0	0.1	0.2	0.0	0.0	0.1	0.1	0.1	0.0	0.0	0.0	0.0
	copper	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.0	0.0	0.0	0.0
	iron	0.2	0.1	0.1	0.2	0.1	0.0	0.1	0.2	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0
	aluminum	0.2	0.1	0.1	0.2	0.1	0.0	0.1	0.2	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0
	Initial water-proof of heat-shrink tube	Failure															
	stainless steel	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	copper	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	iron	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	aluminum	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	kg/cm																
	Adhesion strength after 150°C × 3000																
	Water-proof after degradation	Failure															

(note)

(*1) PVdF-1:

Mitsubishi Chemical, trade name "KAYNR 9300" [melting point =100°C, MFR = 120g/min (190°C, 2.16kg)]

(*2) PVdF-2:

Mitsubishi Chemical, trade name -- "KAYNR 7200" [melting point =120°C degree-C, MFR=2g/min (230°C, 2.16kg)]

(*3) FKM-1:E.

I. du Pont de Nemours, trade name "Viton E-430" [fluorine content =66%, Mooney viscosity (ML₁₊₁₀, 121°C) =20]

(*4) FKM-2 :

E. I. du Pont de Nemours, trade name "Viton B-50" [fluorine content =68%, Mooney viscosity (ML₁₊₁₀, 121°C) =30]

Comparative Examples 33 to 44

Procedure of Example 1 was repeated except the fluorine polymer for the adhesive composition and the dose of accelerated electron ray were changed as are shown in Table 6 while a proportion of the polar-group containing unsaturated compound was reduced to less than 2 pars by weight (Comparative Examples 33 o 38) and increased to higher than 30 pars by weight (Comparative Examples 39 o 44). The adhesive composition and the multilayer heat shrink tube were evaluated by the similar methods.

Although not shown in Table 6, 0.5 parts by weight of pentaerythritol-tetrakis [3-(3, 5-di-t-butyl-4-hydroxyphenyl)propionate] was blended as anti-oxidant to each adhesive composition to 100 parts by weight of the fluorine polymer.

Evaluation revealed that all adhesive compositions had poor the initial adhesive strength of lower than 1.0 kg/cm for Comparative Examples 33 to 44. Therefore, degradation test at 150°C, for 3000 hours was not effected.

The multilayer heat shrink tube having the adhesive composition in its inner layer of Comparative Examples 33 to 44 failed to the initial waterproof evaluation test. It is clear that these products can not passed the waterproof evaluation test after degradation. Result is summarized in Table 6.

[Table 6]

(note)

(*1) PVdF-1:

Mitsubishi Chemical, trade name "KAYNR 9300" [melting point = 100°C, MFR = 120g/min (190°C, 2.16kg)]

(*2) FKM-1:E.

I. du Pont de Nemours, trade name "Viton E-430" [fluorine content = 66%, Mooney viscosity (ML₁₊₁₀, 121°C) = 20]

Comparative Examples 45 to 56

Procedure of Example 1 was repeated except blends of fluorine polymer were used the dose of accelerated electron ray were changed as are shown in Table 7 while a proportion of the polar-group containing unsaturated compound was reduced to less than 2 parts by weight (Comparative Examples 45 to 50) and increased to higher than 30 parts by weight (Comparative Examples 51 to 56). The adhesive composition and the multilayer heat shrink tube were evaluated by the similar methods.

Although not shown in Table 7, 0.5 parts by weight of pentaerythritol-tetrakis [3-(3, 5-di-*t*-butyl-4-hydroxyphenyl)propionate] was blended as anti-oxidant to each adhesive composition to 100 parts by weight of the fluorine polymer.

Evaluation revealed that all adhesive compositions had poor the initial adhesive strength of lower than 1.0 kg/cm for all Comparative Examples 45 to 56. Therefore, degradation test at 150°C, for 3000 hours was not effected.

The multilayer heat shrink tube having the adhesive composition in its inner layer of Comparative Examples 45 to 56 failed to the initial waterproof evaluation test. It is clear that these products can not passed the waterproof evaluation test after degradation. Result is summarized in Table 7.

[Table 7]

- (*1) PVdF-2:
Mitsubishi Chemical, trade name -- "KAYNR 7200" [melting point =120°C degree-C, MFR=2g/min (230°C, 2.16kg)]
- (*2) FKM-2 :
E. I. du Pont de Nemours, trade name "Viton B-50" [fluorine content =68%, Mooney viscosity (ML₁₊₁₀, 121°C) =30]

Comparative Examples 57 to 68

Procedure of Example 1 was repeated except the fluorine polymer used for the adhesive composition, the polar-group containing unsaturated compound, blending ratio and the dose of exposure to accelerated electron ray were changed as are shown in Table 8 and the adhesive composition and the multilayer heat shrink tube were evaluated by the similar methods.

Although not shown in Table 8, 0.5 parts by weight of pentaerythritol-tetrakis [3-(3, 5-di-t-butyl-4-hydroxyphenyl)propionate] was blended as anti-oxidant to each adhesive composition to 100 parts by weight of the fluorine polymer.

Evaluation revealed that adhesive compositions Comparative Examples 57 to 62 had poor the initial adhesive strength of lower than 1.0 kg/cm because the dose is lower. Therefore, degradation test at 150°C, for 3000 hours was not effected.

The multilayer heat shrink tube having the adhesive composition in its inner layer of Comparative Examples 57 to 62 failed to the initial waterproof evaluation test. It is clear that these products can not passed the waterproof evaluation test after degradation.

On the other hand, when the dose was increased (Comparative Examples 63 to 68), the adhesive compositions had high initial adhesive strength of higher than 1.0 kg/cm so that the multilayer heat shrink tube having the adhesive composition in its inner layer passed the initial waterproof evaluation test.

However, these adhesive compositions were deteriorated seriously after degradation test 150°C, for 3000 hours and therefore can not pass the waterproof evaluation after degradation. Result is summarized in Table 8.

[Table 8]

(note)

(*1) PVdF-1:

Mitsubishi Chemical, trade name "KAYNR 9300" [melting point = 100°C, MFR = 120g/min (190°C, 2.16kg)]

(*2) FKM-2 :

E. I. du Pont de Nemours, trade name "Viton B-50" [fluorine content = 68%, Mooney viscosity (ML₁₊₁₀, 121°C) = 30]

Example 25

Two-layered structure tube (inner diameter of 2.5 mm, outer diameter of 6.5 mm, and a thickness of the inner layer is 1 mm) was produced by co-extruding following two layers from a cross head of following two melting extruders at 230°C:

- 1) a melting extruder for outer layer (40 mmφ, full flight type of Hastelloy type) which extruded a radiation-induced crosslinkable composition comprising 100 parts by weight of thermoplastic fluoride resin [Sumitomo 3M, trade name "Dyneon"; melting point = 110-130°C, MFR = 20 g /10 minutes (250°C, 5 kg)] and 1 part by weight of trimethylolpropanetrimethacrylate, and
- 2) another melting extruder for inner layer (30 mmφ, full flight type of Hastelloy type) which extruded pellets of the composition containing the terpolymer prepared in Example 1, glycidyl methacrylate and antioxidant.

The resulting two-layered tube was irradiated with electron ray at acceleration voltage of 2 MeV at a dose of 60 kGy to effect crosslinking of the outer layer and graft-denaturing of the inner layer.

The resulting crosslinked tube was pre-heated in a thermostat at 150°C for 3 minutes and then was expanded by feeding compressed air into the tube to an outer diameter of 6.5 mm. Then, the tube was taken out of the thermostat immediately and was immersed in water to set or solidify the shape (Fig. 1).

The resulting multilayer heat shrink tube was cut to a length of 30 mm and was put on a cylindrical rod having a diameter of 6.0 mm and made of tetra fluoride resin, as is shown in Fig. 2, in such a manner that a length of 20 mm covers the cylindrical rod. Then, an assembly was left in a thermostat at 150°C for 3 minutes so that the tube shrinks to obtain a heat shrink cap having a configuration of Fig. 3 in which the inner layer adhesive composition was welded to close the cap.

Evaluation of waterproof

Each coating layer of three fluorine wires of Sumitomo Electric Industries Ltd (ARX-3KAI) each having an outer diameter of 1.48 mm (conductor = 11/0.16, thickness = 0.43mm) was removed at its end at a length of 5 mm and three wires were clipped by a metal end cap (outer diameter pf 4.00 mm). Onto this end cap, the multilayer heat shrink tube of above-mentioned was put, as is shown in Fig. 4, and an assembly was left in a thermostat at 150°C for 3 minutes so that the tube shrinks to obtain a joint sample.

The joint sample was immersed in a 5% aqueous solution of sodium chloride in

a tank and left at room temperature for 1 hour. Then, DC 500V was impressed between conductors of the wires and a counter electrode installed in the tank to measure a resistance. It was confirmed that the resistance was higher than 100 M Ω which means that sufficient water-tightness was assured.

The same waterproof evaluation was effected after degrading of the joint under the condition of 150°C, for 3000 hours to find sufficient water-tightness of post acceleration degradation.

Availability on industry

The hot melt type adhesive composition of this invention possesses improved adhesion to metallic objects including metallic objects and thermal resistance. The adhesive composition, multilayered heat shrink tube and a heat shrink cap can be used advantageously for protection, connection and hermetic seal of electric wire, wire harness (knitted wires) and piping for which high continuous thermal resistance of higher than 150°C is requested.

The adhesive composition and products such as heat shrink tube and heat shrink cap of this invention can be used for protection, connection and hermetic seal in all parts in automobile, aircraft and space industries where high continuous thermal resistance of higher than 150°C is requested.

Claim(s)

1. The adhesive composition, containing 100 parts by weight of fluorine polymer and 2 to 30 parts by weight of unsaturated compound having at least one polar group chosen from a group comprising epoxy group and carboxyl group, wherein said fluorine polymer is graft-denatured with said unsaturated compound grafted by exposure to ionized radiation.
2. The adhesive composition according to claim 1, containing further 0.1 to 5 parts by weight of antioxidant with respect to 100 parts by weight of said fluorine polymer.
3. The adhesive composition according to claim 1, wherein said fluorine polymer is selected from fluoride resin and fluoride rubber.
4. The adhesive composition according to claim 1, wherein said fluoride resin has a fusion point of 80 to 140°C and said fluoride rubber has a Mooney viscosity (ML₁₊₁₀, at 121°C) of 5 to 70.
5. The adhesive composition according to claim 3, wherein said fluoride resin is selected from a group comprising polyvinylidene fluoride (PVdF); copolymer (VdF-TFE) of vinylidene fluoride (VdF) and tetrafluoroethylene (TFE); copolymer (VdF-HFP) of vinylidene (VdF) and hexafluoropropylene (HFP); terpolymer (VdF-TFE-HFP) of vinylidene fluoride (VdF), tetrafluoroethylene (TFE) and hexafluoropropylene (HFP); copolymer (ETFE) of ethylene and tetrafluoroethylene (TFE); copolymer (ECTFE) of ethylene and chlorotrifluoroethylene; copolymer (FEP) of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP) and a copolymer (PFA) of tetrafluoroethylene (TFE) and perphloro alkyl vinyl ether (PFA).
6. The adhesive composition according to claim 3, wherein said fluoride rubber is selected from a group comprising copolymer (VdF-HFP) of vinylidene fluoride (VdF) and hexafluoropropylene (HFP); copolymer (VdF-HFP-TFE) of vinylidene fluoride (VdF), hexafluoropropylene (HFP) and tetrafluoroethylene (TFE); copolymer (VdF-PFP) of vinylidene fluoride (VdF) and pentafluoropropylene (PFP); copolymer (VdF-PFP-TFE) of vinylidene fluoride (VdF), perfluoromethylvinylether (PFMVE) and tetrafluoroethylene (TFE); copolymer (VdF-CTFE) of vinylidene fluoride (VdF) and chlorotrifluoroethylene (CTFE); copolymer (TFE-P type fluorine rubber) of tetrafluoroethylene (TFE) and propylene; and thermoplastic fluorine rubbers.
7. The adhesive composition according to claim 1, wherein said unsaturated compound having epoxy group has, in its molecular, at least one epoxy group and polymerable carbon-carbon unsaturated bond.

8. The adhesive composition according to claim 7, wherein said unsaturated compound having epoxy group is selected from a group comprising glycidyl esters, allyl glycidyl isocyanate, mono or poly- glycidyl esters of unsaturated poly carboxylic acids and allyl glycidyl ethers.
9. The adhesive composition according to claim 7, wherein said allyl glycidyl ester is glycidyl methacrylate and said allyl glycidyl isocyanate is diallyl monoglycidyl isocyanate.
10. The adhesive composition according to claim 1, wherein said unsaturated compound having carboxyl group has, in its molecular, at least one carboxyl group or anhydride group and polymerable carbon-carbon unsaturated bond.
11. The adhesive composition according to claim 10, wherein said unsaturated compound having carboxyl group is selected from a group comprising unsaturated carboxylic acid, anhydride of unsaturated dicarboxylic acid and anhydride of unsaturated monocarboxylic acid.
12. The adhesive composition according to claim 11, wherein said unsaturated compound maleic anhydride.
13. The adhesive composition according to claim 11, wherein said fluorine polymer is graft-denatured with said unsaturated compound grafted by exposure of ionized radiation at a doze of 20 to 700 kGy.
14. The adhesive composition according to claim 1, possessing the initial adhesive strength by T-peel test of higher than 1.0 kg/cm for all metal plates selected from a group comprising stainless, copper , iron and aluminum plates when said adhesive composition is bonded to a test sample of said metal plate having a thickness of 1 mm and peeled at a rate of 50 mm/min.
15. The adhesive composition according to claim 1, possessing an aged adhesive strength by T-peel test of higher than 1.0 kg/cm for all metal plates selected from a group comprising stainless, copper , iron and aluminum plates when said adhesive composition is bonded to a test sample of said metal plate having a thickness of 1 mm, followed by aging in an oven of 150°C for 300 heures and then peeled at a rate of 50 mm/min.
16. A molded article having an adhesive layer of said adhesive composition defined in any one of claims 1 to 16.

17. A multilayered heat shrink tube having an adhesive layer of said adhesive composition defined in any one of claims 1 to 16 as an inner layer.

18. A heat shrinkable cap having a structure of a multilayered heat shrink tube having an adhesive layer of said adhesive composition defined in any one of claims 1 to 4 as an inner layer, said a multilayered heat shrink tube having an opening at one end, so that seal is effected with adhesive composition when said when the tube is heat-shrunk and

19. A process for preparing adhesive composition containing a fluorine polymer, comprising

- (i) preparing adhesive composition, containing 100 parts by weight of fluorine polymer and 2 to 30 parts by weight of unsaturated compound having at least one polar group chosen from a group comprising epoxy group and carboxyl group, and then
- (ii) said fluorine polymer is graft-denatured with said unsaturated compound grafted by exposure to ionized radiation, optionally after said composition is shaped.

20. A process for preparing a multilayer heat shrink tube, comprising

- (1) preparing a two-layered heat shrink tube by co-extruding an inner layer of the fluorine polymer composition, and an outer layer of radiation-crosslinkable composition containing 100 parts by weight of fluorine polymer and 2 to 30 parts by weight of unsaturated compound having at least one polar group chosen from a group comprising epoxy group and carboxyl group,
- (2) irradiating said two-layered heat shrink tube with ionizing radiation to effect radiation-induced crosslinking of said outer layer and to effect graft-denaturing of said inner layer of fluorine polymer composition,
- (3) expanding the tube radially under heat, and
- (4) cooling the tube to fix its configuration expand radially.

图1

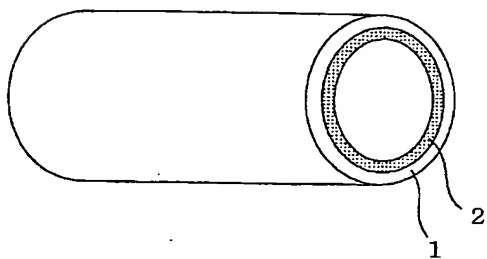


图2

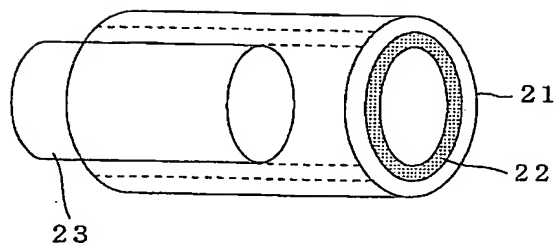


图3

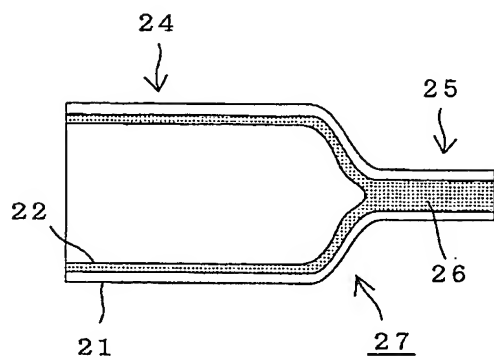
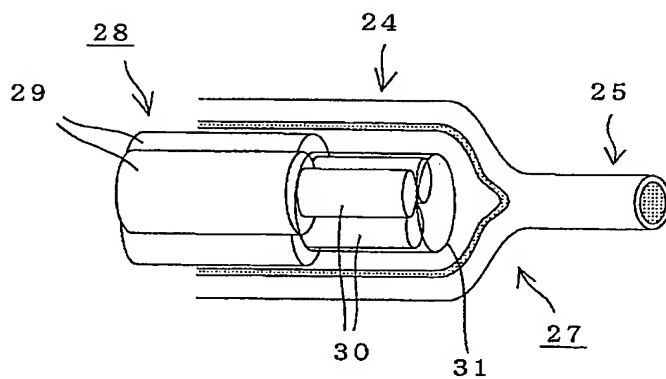


图4



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JUN 22 2006

ARKEMA INC.
LAW DEPARTMENT

Thierry SENNINGER

20/06/2006 16:00

To: Thomas ROLAND
Subject: duty of disclosure

Tom,

I forward you by mail the translation of WO 2005/005564 from Sumitomo Electric Fine Polymer (I have not found the electronic copy). This document should be disclosed to the Examiner for the following cases:

AM 2003
AM 2068
AM 2069
AM 2142

It relates to the grafting of an unsaturated monomer onto a fluoropolymer. It might be bothering for us.

Best regards,

Thierry SENNINGER, Dr.Sc.

ARKEMA

Intellectual Property Department

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